

Permeation of Propane and Propylene through Cellulosic Polymer Membranes

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Synopsis

Cellulosic polymers were tested by measuring their permeabilities of propane and propylene. High permeabilities and selectivities were obtained with ethyl cellulose membranes. Hollow fibers coated with ethyl cellulose were made through a solution coating method. Microporous polypropylene hollow fibers were used as base material. A dense layer of ethyl cellulose about 6–10 μm in thickness was formed on the microporous hollow fiber. The performance of a coated membrane column was tested for the separation of propane and propylene mixture gas. It was concluded that ethyl cellulose membranes have a good potential for the separation of olefins from saturated hydrocarbons.

INTRODUCTION

The permeability of gases and vapors through polymer films has been studied for a great many systems. Most of these studies, however, have been concerned with the permeation of permanent gases. To develop the application of membrane separation process for industrial gases, more permeation data on hydrocarbons through polymer films are needed. The separation of propane and propylene, in particular, is of great importance to the petroleum industry because the relative volatility of this system is rather small. Since the permeabilities of these hydrocarbons through glassy polymers are generally too low to measure, there have been very little literature on the permeation of propane and propylene through polymer membranes. Only for the case of polyethylene films, the permeabilities of these gases were measured by Henley and Santos.¹ They pointed out an interesting behavior of the permeabilities that separation factor increases in the low temperature range. Their separation factor, however, was insufficient to separate these gases. Although the permeabilities of propane through polymer membranes have been reported by some investigators,^{2–4} no other study was available on the separation factor of propane and propylene through polymer membranes. Furthermore, there are no reports on permeation of gas mixtures that are of practical importance in petrochemical industry.

There are two essential requirements in order for membrane process to be employed for propane–propylene separation. One is to find a polymer material that has both high permeability and high selectivity toward this system. The

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TABLE I
The Permeabilities^a of Propane and Propylene through Hollow-Fiber Membranes
at Selected Temperatures

Temperature		CA	Polysulfone ^b	Silicone rubber
40°C	Propane	0.320	2.63	649
	Propylene	1.21	3.75	644
-17°C	Propane	0.450	3.16	2950
	Propylene	0.398	3.41	1520
OD/ID (mm)		0.26/0.12	0.25/0.094	0.33/0.17
Δp (cm Hg)		151.5	76.5	151.5

^a $\times 10^{-9}$ cm³ (STP) cm/s cm² cm Hg.

^b Though the polysulfone hollow fibers were asymmetric type, the permeabilities were based on the wall thickness of the hollow fiber because of the difficulty to measure the effective thickness of the skin layer.

other is to develop a method to make thin membranes. The present study addresses both of these points. Various polymer materials were tried to see if any of them were suitable for propane and propylene separation. The effects of heat or cold treatment on the permeability of cellulosic polymer membranes were also investigated. A coating method was developed by applying polymer solution on a microporous hollow fiber to make a dense skin layer. Then a coated membrane column was constructed and tested for the separation of propane and propylene mixture gas.

PERMEABILITY MEASUREMENTS WITH HOLLOW-FIBER COLUMN

Since propylene permeation data had been lacking for many polymeric materials, three commercial hollow fibers—cellulose acetate (CA), polysulfone, and silicone rubber—were tested. The cellulose acetate hollow fibers were obtained from the Max-Planck-Institute for Biophysics, Frankfurt a.m., West Germany. The permeabilities of propane and propylene through these membranes were measured in a temperature range from -17 to 80°C. The permeabilities of propane and propylene at selected temperature are shown in Table I. Figure 1 shows temperature dependence of the ideal separation factor α , the ratio of permeabilities of propane and propylene, through the hollow-fiber columns of these polymers. These results indicate that cellulose acetate was the one of promising materials for our purpose. This column exhibits a separation factor of 2.7 at 20°C and 4.8 at 80°C.

The experimental conditions for obtaining these data will be briefly discussed. This cellulose acetate column was made by the nontreated hollow fibers that had been stored in room air. In the early stage of measurement, this column exhibited no permeation of propane or propylene in a temperature range from 60 to -17°C. After maintaining the condition of -17°C for 3 h, however, permeability was markedly improved, which is shown in Figure 1. Therefore, it can be concluded that the increase in permeability is caused by some change of polymer structure through the low-temperature treatment.

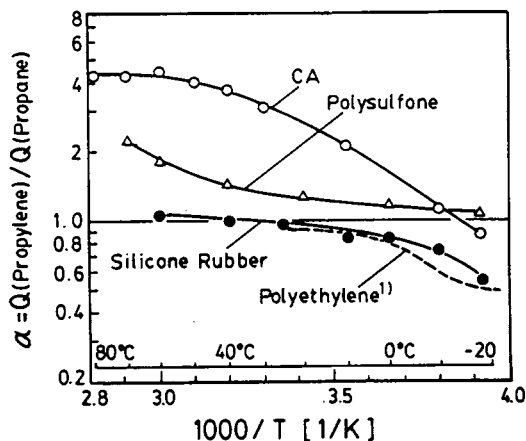


Fig. 1. The ideal separation factors of CA, polysulfone, and silicone rubber membranes.

PERMEABILITY MEASUREMENTS WITH CAST CELLULOSIC MEMBRANES

After the permeation experiments of the above hollow fibers, four cellulosic polymers—CA, cellulose triacetate (CTA), celluloseacetate butylate (CAB), and ethyl cellulose (EC)—were selected for further study. Dense membranes of 0.003–0.012 mm thickness were prepared by casting 5–10% solution in dioxane for CA, CAB, EC, or in chloroform for CTA on a glass plate using a Gardner knife. The thickness of film was determined by weighing known amount of membrane area. The membrane thickness had to be greater than 0.003 mm to avoid any pinholes that destroyed the selectivity of membrane. Permeation measurements were performed with a high-pressure cell at room temperature. Upstream and downstream were maintained 3 and 1 atm, respectively. Permeation area was 13.2 cm². Permeation rates were measured by volume displacement using a soap bubble meter.

Some membrane samples were further treated and measured for their permeabilities. Dry treatment was made by drying of a sample in a 80°C oven for 3 h. Low-temperature treatment was made by placing the permeation cell, which held a membrane sample, in a refrigerating circulator at a temperature of –20°C. This condition was maintained for 4 h.

Resulting permeabilities are shown in Figure 2. There were appreciable differences in permeability measurements for each sample of the same material but with different and casting condition. Typical results among several samples are shown in this figure.

CAB and EC exhibits high permeabilities of propane and propylene. EC also has high selectivity of 5–6. On the other hand, the permeabilities through nontreated CA and CTA films were not measurable by this simple method. It means that their permeabilities are lower than 1×10^{-11} cm³ (STP) cm/cm² s cm Hg. These results agree with the experimental values by Gantzel and Merten⁴ (lower than 1×10^{-11}) and that by Haraya et al.² (3×10^{-13}) on the permeabilities of propane through dense CA membranes.

Figure 2 also shows the changes of permeabilities for cast membranes by low-temperature treatments (L) and high-temperature treatment (H). The

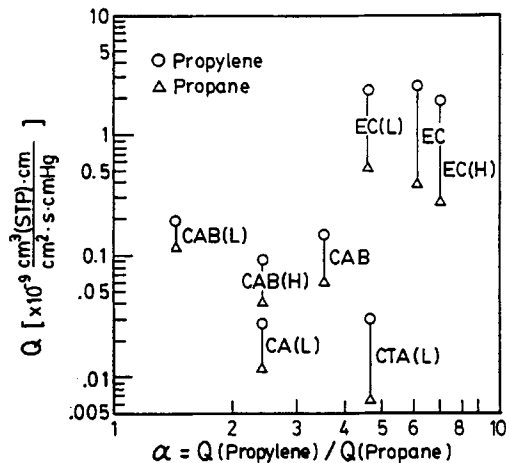


Fig. 2. Permeabilities of propane and propylene through cast membranes of cellulosic polymers.

permeabilities through CA and CTA membranes appear to increase by the low-temperature treatment as much as 10 times compared to those through nontreated membranes. The separation factors of the low-temperature treated CA membranes were around 2.5 which is close to the data for CA hollow fibers shown in Figure 1. The low-temperature treated CTA membranes have larger separation factors than those of CA membranes. Similar effects of the treatments can be observed for EC and CA membranes, but are not obvious. This kind of improvement of permeability through drying at low temperature has been reported for the case of CA asymmetric membrane.^{5,6} We may attribute this phenomena to some change of polymer structure caused by moisture absorbed in CA or CTA and the subsequent low temperature treatment. This explanation is supported by the data that this effect was small for EC of which moisture content is small.

MIXTURE GAS SEPARATION WITH ETHYL CELLULOSE COATED HOLLOW-FIBER MODULE

It was intended to test the separation performance of ethyl cellulose membranes to the mixed gas. For this purpose, a hollow-fiber module was needed to collect enough permeate gas for analysis by gas chromatography.

Ethyl cellulose hollow fibers were made by the Celgard solution coating method. Microporous polypropylene hollow fibers and Celgard X-10 (Celanese Separation Products, Charlotte, NC) were selected as base material. The dioxane solution of ethyl cellulose was coated at a constant rate following which it was immediately dried by hot air. A layer of ethyl cellulose of 0.006–0.01 mm thickness was formed on the microporous hollow fiber by this method. The module consisted of 40 fibers. Permeation area was about 110 cm². The column was operated at the same pressure conditions as the permeation cell mounted with cast membrane. Analysis of binary mixtures was performed on a gas chromatograph with Sebaconitril columns. The pressure drop along the column was negligible.

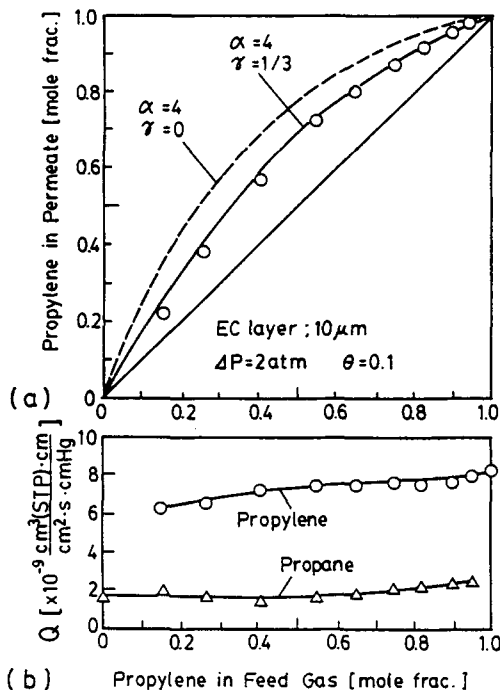


Fig. 3. Permeation of mixed gas through EC coated hollow fibers.

Figure 3(a) shows the permeate concentrations at various feed gas concentrations. The ideal separation factor, the permeability ratio of propane and propylene, of this module was 4.1 which is lower than that of the cast dense membrane. The permeabilities of these pure gases through the module were greater than those of dense membrane, and they are shown in Figure 5. This decline of separation factor and the increase of permeability of each gas for coated membranes may have been caused by the difference in the amounts of solvent evaporation between the cast film and the coated membrane. For the case of dense cast film on glass plate, the surface attached on glass plate is much denser than the other surface open to air, because the solvent evaporates only through air side surface. For the case of coated polymer membrane on the outside of hollow-fiber, solvent may evaporate through inside of polymer layer attached on the microporous hollow fiber as well as through outside of coated layer. Then the polymer layer structure of coated membrane may be less tight than that of cast film on glass plate.

The solid line in Figure 3(a) is calculated from the pure gas permeabilities and the pressure ratio across the membrane using the following equation:

$$y = \frac{(\alpha - 1)(\phi + x) + 1 - \left\{ [(\alpha - 1)(\phi + x) + 1]^2 - 4\phi(\alpha - 1)\alpha x \right\}^{1/2}}{2\phi(\alpha - 1)} \tag{1}$$

where $\phi = \theta + \gamma(1 - \theta)$. The dashed curve in the figure represents the maxi-

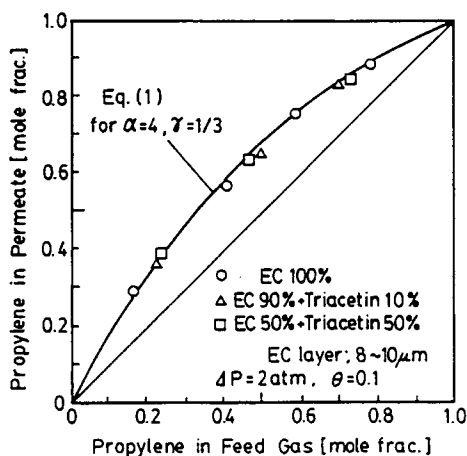


Fig. 4. The effect of plasticizer.

imum attainable concentration by this column. It appears that the experimental data match very well with the calculated results based on the pure gas permeabilities.

The permeabilities of individual components in mixture permeation experiments were evaluated based on the partial pressure differences. These are plotted in Figure 3(b). The permeabilities to the mixed gases increased for propane and decreased for propylene in a high concentration range of the other component. As Seok et al.⁷ discussed for a glassy polymer membrane (cellulose acetate), the presence of hydrocarbon in the mixed gas can affect both fast and slow gas permeabilities. This effect was not so large in the separation performance of the column.

There is a practical difficulty in fabricating an ethyl cellulose membrane because of its brittleness. To improve mechanical strength of the membrane, a plasticizer, triacetin, was mixed in the polymer solution and coatings were made by this solution. The effect of plasticizer in ethyl cellulose on separation performance is shown in Figure 4. A series of separation experiments were conducted by using the coated polymer membranes containing 10 and 50 wt % of triacetin. There is no appreciable effect on the separation data due to a different amount of plasticizer. Consequently, a plasticizer can be used in practice without comprising the separation property of ethyl cellulose.

Figure 5 shows the temperature effect on the permeability of pure propane and propylene for cast EC membrane and coated EC hollow fibers. In the case of cast membrane, the permeabilities for both gases first decrease and then increase as temperature decreases progressively. A similar behavior has been observed for the permeation of methyl bromide, isobutene,⁸ and propane¹ through polyethylene films. This type of permeability change vs. $1/T$ is attributed to a plasticization-condensation phenomenon.¹ The maximum separation factor was obtained near 0°C for cast membrane. On the other hand, temperature dependency is not pronounced in the case of coated membrane.

The results of mixture gas permeations with the hollow-fiber column are shown in Figure 6. In agreement with the pure gas permeability data there is no significant effect of temperature on separation performance of mixed gases in a temperature range from 60 to 0°C.

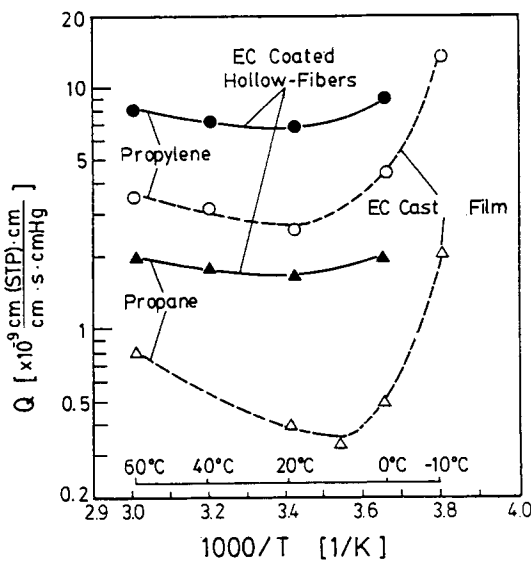


Fig. 5. The effect of temperature on the permeabilities of propane and propylene (high pressure side 3 atm, low pressure side 1 atm).

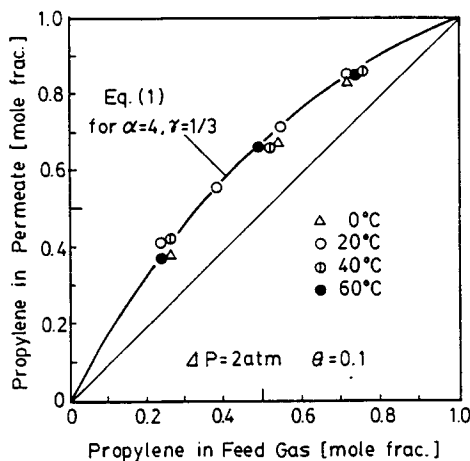


Fig. 6. The effect of temperature on mixture gas permeation.

CONCLUSION

Selected materials of cellulosic polymers were tested by measuring their permeabilities of propane and propylene. The highest permeabilities and selectivities were obtained with ethyl cellulose membranes. For the case of cellulose acetate and cellulose triacetate, a low-temperature treatment was quite effective to increase the permeability of propylene. The usefulness of a coated membrane column was demonstrated for the separation of propane and propylene mixture. Although more development of coating technique would be necessary to improve separation efficiency to approach to large as that of cast membrane, ethyl cellulose was shown to be quite promising for the separation of propylene from propane.

APPENDIX: NOMENCLATURE

- P pressure
 Q permeability (cm^3) (STP) $\text{cm}/\text{cm}^2 \text{ s cm Hg}$
 T temperature (K)
 x mole fraction of more permeable gas in feed stream
 y mole fraction of more permeable gas in permeate
 α ideal separation factor
 γ pressure ratio of permeate side to feed side
 θ cut, permeation rate/feed flow rate

This article is based upon work supported under a grant for The Center-of-Excellence for Membrane Technology. Also, the authors are grateful for supplying the membrane samples by Dr. W. Pusch, Max-Planck-Institute for Biophysics, Frankfurt a.m., West Germany.

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Received September 1, 1988

Accepted September 15, 1988